Enhanced Bioremediation Technologies

Victor Magar, Ph.D., P.E.
and
Bruce Alleman, Ph.D.
Battelle Memorial Institute

Enhanced Bioremediation Technologies:
Definition

- Engineered Applications Designed to Stimulate Biological Transformations of Contaminants in Groundwater

Enhanced Bioremediation Technologies:

Technology Progression

Contaminant	Stage	Technologies
Petroleum Hydrocarbons	Conventional	Biopile Composting Land Farming Bioslurry Reactors Bioventing Bioslurping
Petroleum Hydrocarbons	Innovative	Air Sparging Monitored Natural Attenuation (Petroleum Hydrocarbons)
Chlorinated Hydrocarbons	Innovative	Monitored Natural Attenuation (Chlorinated Hydrocarbons)
Chlorinated Hydrocarbons	Emerging	Enhanced Anaerobic Dechlorination (EAD) Anaerobic Bioventing Sequential Anaerobic/Aerobic Treatment In Situ Cometabolism Cometabolic Air Sparging (CAS)
Chlorinated Hydrocarbons	Early Development	Bioaugmentation Bioengineering (GEMs)

Enhanced Bioremediation Technologies:
Outline

I. Bacterial Metabolism and Growth

II. Respiratory Processes and Metabolism

III. Biotreatment of Major Groundwater Contaminants

IV. Biodegradation/Biotransformation of Chlorinated Aliphatic Hydrocarbons (CAH)

V. Anaerobic/Aerobic Technologies and Applications

VI. Case Histories

VII. Tech Transfer (SOW, Cost Estimator, Design Manual, TDS)

Enhanced Bioremediation Technologies:
Bacterial Metabolism and Growth

Substrates
(e.g., contaminants)

CATABOLISM
Energy generation

Products
(e.g., CO_2, H_2O)

ATP
⇅
Membrane potential

ANABOLISM
Energy consumption

Biosynthesis

Simple
compounds
(e.g., amino acids, lipids)

Cellular
constituents
(Biomass)

Enhanced Bioremediation Technologies:

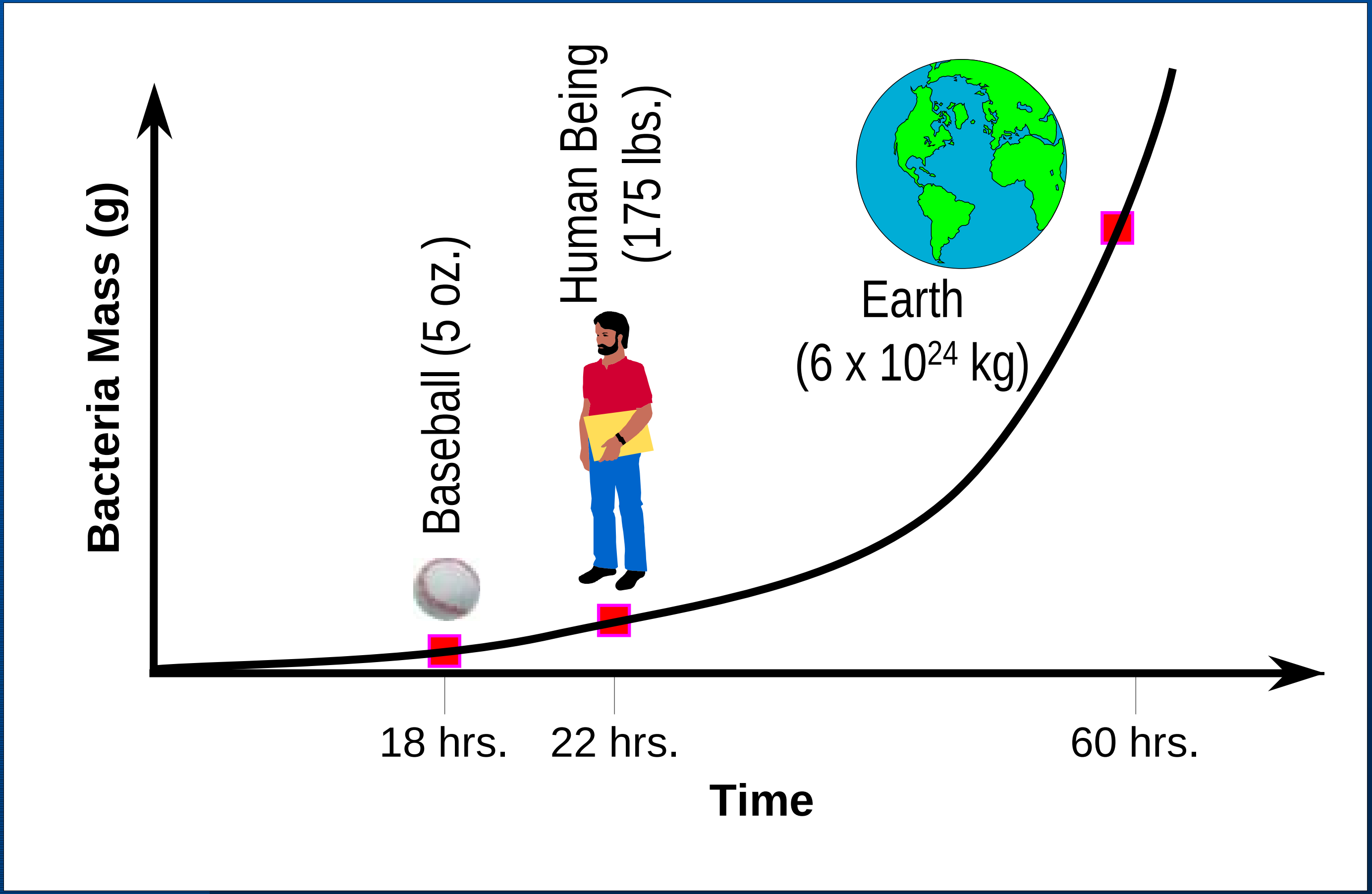
Bacterial Metabolism and Growth (Cont.)

- Bacterial Growth
  - Cell Division: 20- to 30-minute doubling time (optimal)
  - Single Bacterium: 1 million offspring in 10 hrs, in 2 mL of medium

Enhanced Bioremediation Technologies:

Bacterial Metabolism and Growth (Cont.)

Bacterial Growth:
Start w/ a single bacterium (2 x 10^{-9} g); 30-minute doubling time



Enhanced Bioremediation Technologies:

Bacterial Metabolism and Growth (Cont.)

- Bacterial Growth
  - Cell Division: 20- to 30-minute doubling time (optimal)
  - Single Bacterium: 5 billion offspring in 6 to 10 hrs, in 2 mL of medium
- Why don't we see unlimited growth?
  - Requires unlimited nutrient and substrate supply, which rarely occurs in the environment
  - Assumes an unchanging environment
  - Model does not include cell death

Enhanced Bioremediation Technologies:
Outline

I. Overview of Microbiology

II. Respiratory Processes and Metabolism
   - A. Oxidation-Reduction Reactions
   - B. Aerobic Respiration
   - C. Anaerobic Respiration
   - D. Summary

III. Biotreatment of Major Groundwater Contaminants

IV. Biodegradation/Biotransformation of Chlorinated Aliphatic Hydrocarbons (CAH)

V. Anaerobic/Aerobic Technologies and Applications

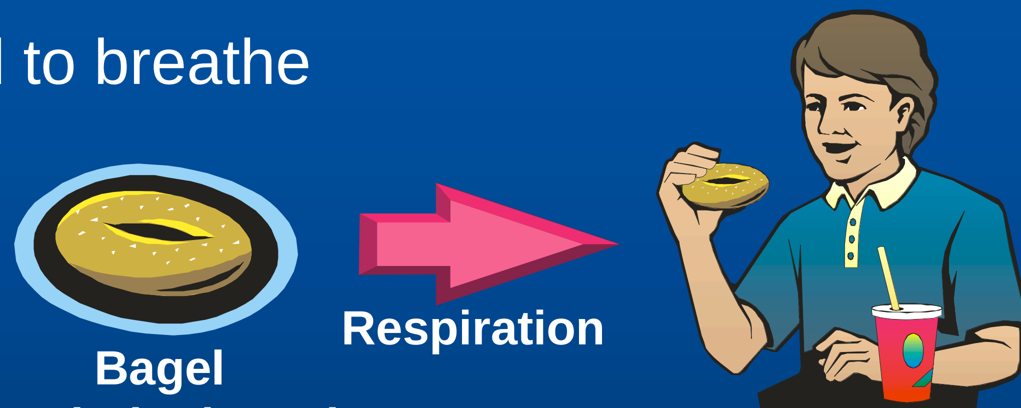
VI. Case Histories

VII. Tech Transfer (SOW, Cost Estimator, Design Manual, TDS)

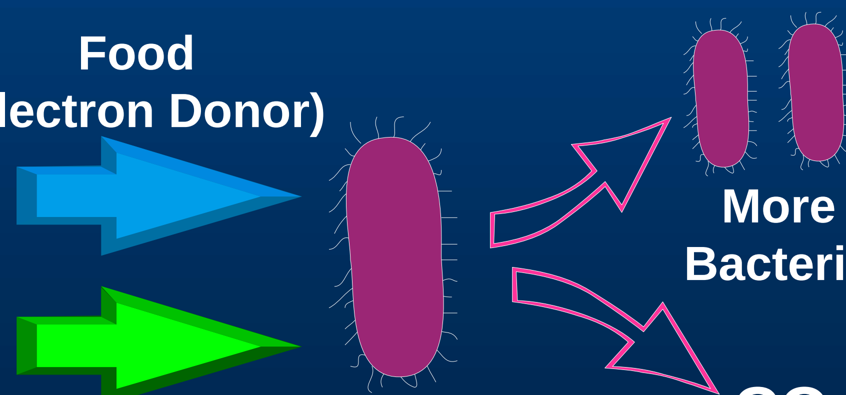
Enhanced Bioremediation Technologies:
Biological Respiration

Respiration: Bacteria need to breathe

<u>Humans</u>
- Carbon source: Food
- Energy source (e^- donor): Food
- Respiration (e^- acceptor): Oxygen
- Nutrients: Food and vitamins
- Water: Food or drink



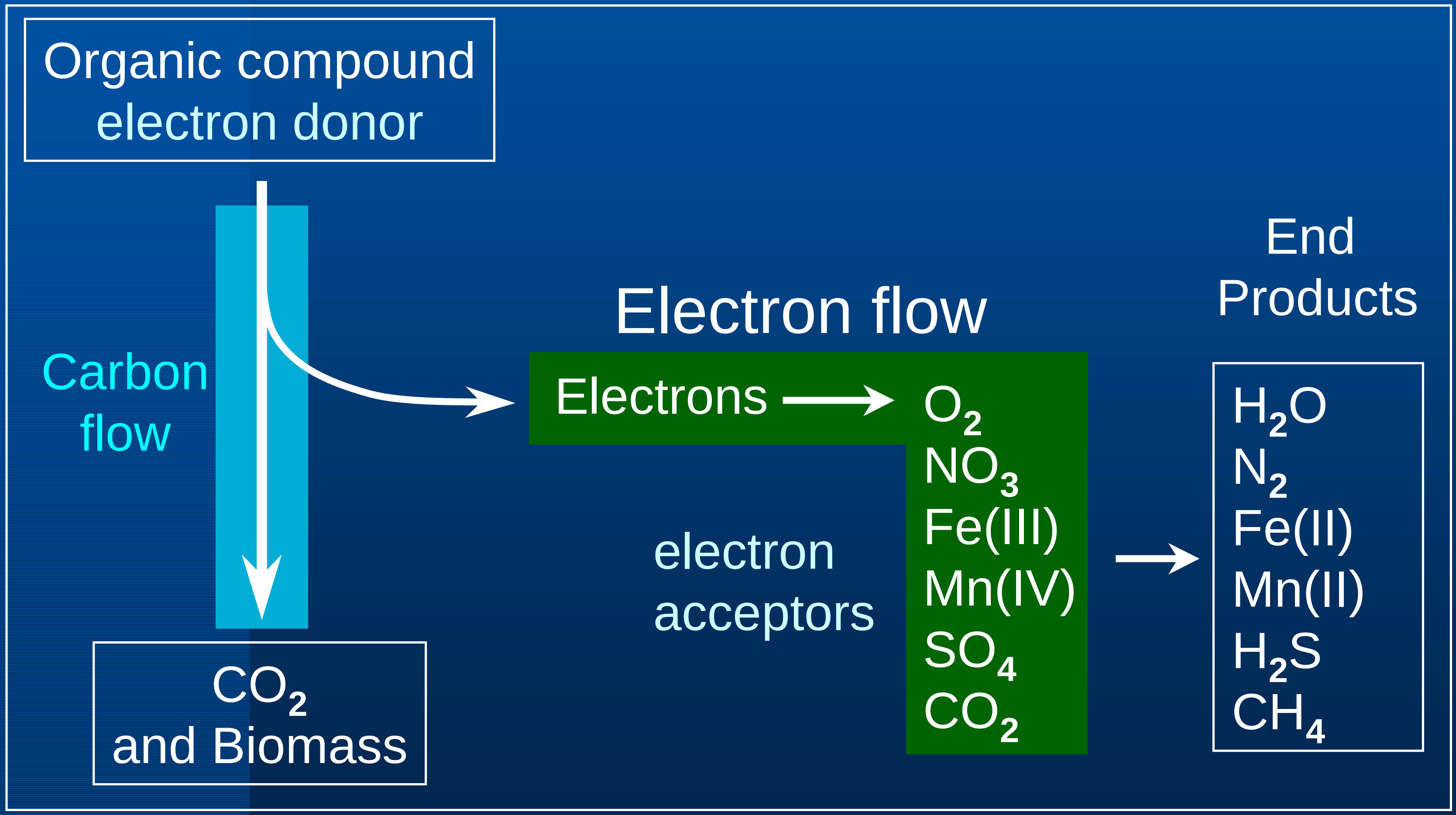
<u>Bacteria</u>
- Carbon source: Organic carbon
- Energy source (e^- donor): Organic carbon
- Respiration (e^- acceptor): Oxygen (aerobic); others (anaerobic)
- Nutrients: Nitrogen, phosporous, minerals
- Water: Groundwater or soil moisture



Enhanced Bioremediation Technologies:
Biological Respiration (Cont.)

- Oxidation-Reduction (Redox) Reactions: What is an Electron Donor/Electron Acceptor?
  - Bacteria require electrons for energy (Electron Donor)
    - When organic matter (carbon) is oxidized it loses an electron (CO_2 is the most oxidized form of carbon)
    - Energy released in the form of electrons
    - Bacteria use the electrons to produce energy
  - Bacteria require an electron sink (Electron Acceptor)
    - When electron acceptors gain electrons they become reduced

Enhanced Bioremediation Technologies:
Biological Respiration (Cont.)



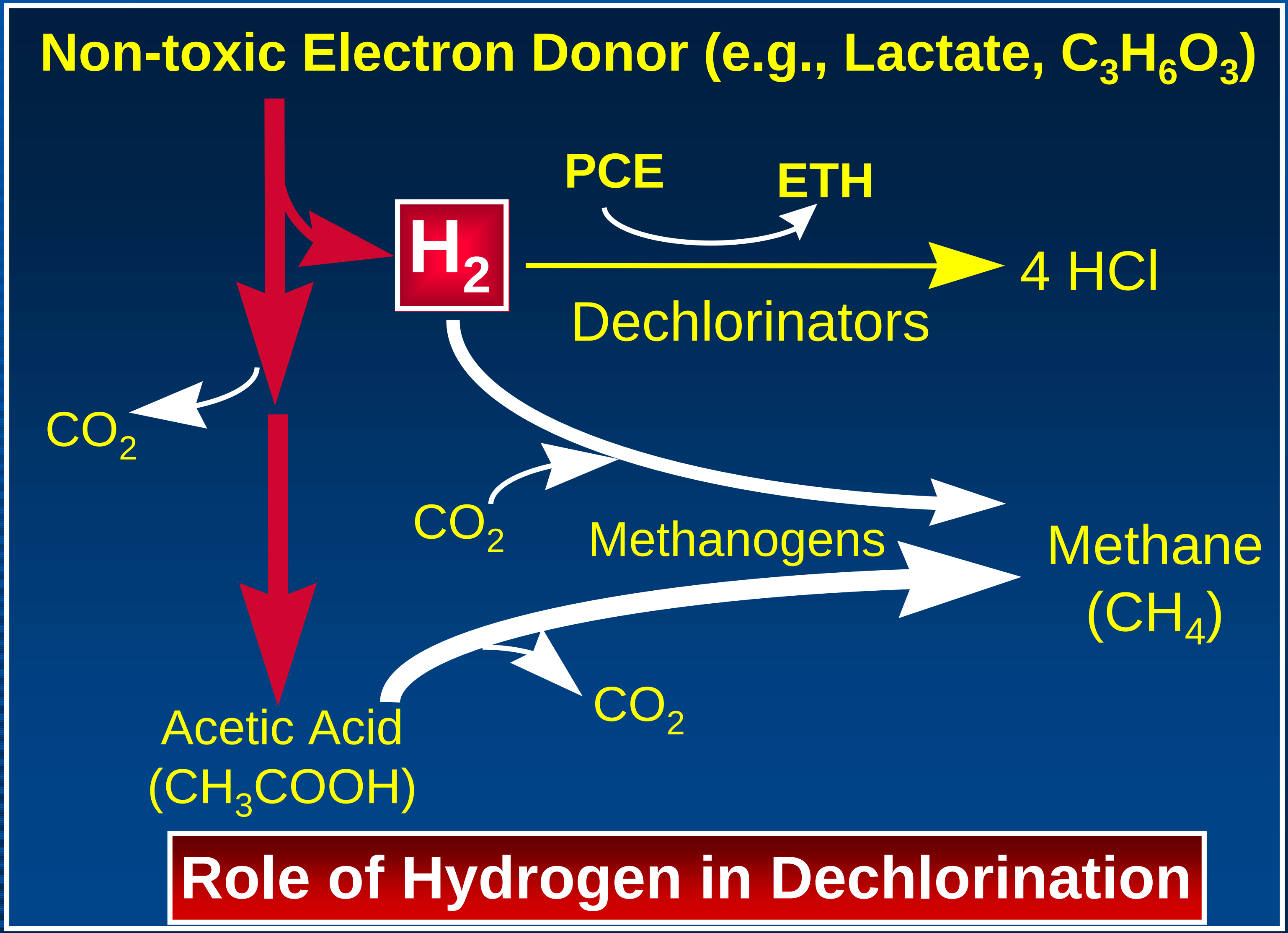
Enhanced Bioremediation Technologies:
Biological Respiration (Cont.)

- Aerobic Respiration
  - Electron Donor: Organic Compound (e.g., contaminant)
  - Electron Acceptor: Oxygen (DO, in water)
- Anaerobic Respiration

Enhanced Bioremediation Technologies:
Biological Respiration (Cont.)

- Aerobic Respiration
- Anaerobic Respiration
  - Organic Electron Donor: Organic Compound (e.g., contaminant or alternative food source added to groundwater)
  - Inorganic Electron Donor: Hydrogen (H_2)
  - Electron Acceptors:
    - NO_3^- (nitrate reduction)
    - Fe^{3+} (iron reduction)
    - Mn^{4+} (manganese reduction)
    - $SO_4^=$ (sulfate reduction)
    - CO_2 (methanogenesis)
    - Halogenated Contaminant (halorespiration)

Enhanced Bioremediation Technologies:
Biological Respiration (Cont.)



Enhanced Bioremediation Technologies:
Example Equations

- Respiratory process: Halorespiration
  - e– donor: Lactate
  - e– acceptor: Chloroethenes

- Lactate fermentation:

Lactate   Acetic Acid

$$C_3H_6O_3 + H_2O \rightarrow CH_3COOH + CO_2 + 2H_2$$

- PCE dechlorination to ethene:

PCE   Ethene

$$C_2Cl_4 + 4H_2 \rightarrow C_2H_4 + 4HCl$$

- PCE + 2Lactate + $2H_2O \rightarrow$ Ethene + 2Acetic Acid + $2CO_2$ + 4HCl

Enhanced Bioremediation Technologies:
Biological Respiration (Cont.)

Electron Tower

Order of e^- Acceptor Depletion

Aerobic

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Anaerobic

$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$

$MnO_2(s) + HCO_3^- + 3H^+ + 2e^- \rightarrow MnCO_3(s) + 2H_2O$

$FeOOH(s) + HCO_3^- + 2H^+ + e^- \rightarrow FeCO_3 + 2H_2O$

$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$

$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$ (Methanogenesis)

Haloresipiration

Enhanced Bioremediation Technologies:
Biological Respiration (Cont.)

NAS Fallon Enhanced Anaerobic Dechlorination Study

- Target contaminant: PCE
- Electron donors: Lactate or benzoate + EtOH
- Sulfate: >10,000 mg/L

Enhanced Bioremediation Technologies:
Biological Respiration (Cont.)

NAS Fallon Enhanced Anaerobic Dechlorination Study

- Observations
  – Redox reduction from +100 to –300 mV
  – Iron sulfide precipitation indicates sulfate reduction
  – Methanogenesis: minimal
  – PCE dechlorination: minimal
- Conclusions
  – e^- donor addition stimulated significant biological activity
  – High sulfate inhibited PCE dechlorination
  – Confirmed by others in laboratory microcosms

Enhanced Bioremediation Technologies:
Biological Respiration (Summary)

- Bacteria need carbon and energy for growth
- Bacteria use electrons for energy (respiration)
  - The source of electrons is the electron donor
- This process requires an electron sink
  - The electron sink is the electron acceptor
- Aerobic electron acceptor is oxygen (O_2/DO)
- Anaerobic electron acceptors
  - NO_3^-, Fe^{3+}, Mn^{4+}, $SO_4^=$, CO_2
  - Halogenated Compounds can serve as electron acceptors under appropriate conditions

Enhanced Bioremediation Technologies:
Outline

I. Overview of Microbiology

II. Respiratory Processes and Metabolism

III. Biotreatment of Major Groundwater Contaminants

  A. Objectives of Engineered Bioremediation

  B. Biotreatment of Major Groundwater Contaminants

IV. Biodegradation/Biotransformation of Chlorinated Aliphatic Hydrocarbons (CAH)

V. Anaerobic/Aerobic Technologies and Applications

VI. Case Histories

VII. Tech Transfer (SOW, Cost Estimator, Design Manual, TDS)

Enhanced Bioremediation Technologies:
Objectives of Engineered Bioremediation

- Find the limiting factor(s) for bacterial growth on contaminants
  - Electron acceptor limitations (e.g., insufficient dissolved oxygen [DO] for aerobic processes)
  - Limited presence of contaminant-degrading bacteria (e.g., low biological count)
  - Low contaminant bioavailability (e.g., large-molecular-weight, hydrophobic compounds)
  - Inability for contaminant to be degraded (e.g., PCE cannot be degraded aerobically)
  - Presence of inhibitory substances (e.g., very high contaminant concentrations may be toxic)
  - Electron donors limitations (e.g., insufficient electron donor for halorespiration)
- Engineer a treatment approach that overcomes limiting factors

Enhanced Bioremediation Technologies:

Objectives of Engineered Bioremediation

- Find the limiting factor(s) for bacterial growth on contaminants
- Engineer a treatment approach that maximizes contaminant degradation by overcoming limiting factors

Enhanced Bioremediation Technologies:
Objectives of Engineered Bioremediation

- Engineer a treatment approach that maximizes contaminant degradation by overcoming limiting factors

Limiting Factor	Example	Solution	Example Technology
Electron Acceptor	Insufficient DO	Add oxygen	Bioventing; Sparging
Bacteria	Low biological count	Stimulate growth; Bioaugment	Biostimulation; Bioaugmentation (Innovative)
Bioavailability	Contaminants with low solubility and high sorption	Add surfactants (innovative); More time for biodegradation; Enhance mixing	Surfactant addition; Natural attenuation; Biopile/composting
Inhibition	High DO in a PCE-contaminated aquifer	Remove DO	Biostimulation (e.g., add an organic substrate)

Enhanced Bioremediation Technologies:
Biotreatment of Major Groundwater Contaminants

- Biotransformation of Petroleum Hydrocarbons (briefly described)
  - BTEX
  - TPH
  - PAHs
- Biotransformation/Biodegradation of Chlorinated Aliphatic Hydrocarbons (focus of this talk)
  - Chloroethenes: PCE, TCE, DCE isomers, VC
  - Chloroethanes: 1,1,1- & 1,1,2-TCA, 1,1- and 1,2-DCA
  - Chloromethanes: Chloroform, methylene chloride

Enhanced Bioremediation Technologies:
Biotreatment of Major Groundwater Contaminants

- Petroleum Hydrocarbon Biodegradation
  - Primarily degraded aerobically
    - Air sparging
    - Bioventing
    - Oxygen Release Compounds
  - Increased evidence of anaerobic transformation/degradation
    - Very important for natural attenuation

Enhanced Bioremediation Technologies:
Biotreatment of Major Groundwater Contaminants

- Chlorinated solvent biodegradation/biotransformation
  - Can involve aerobic or anaerobic processes
  - Generalities:
    - Aerobic – CAHs are oxidized to CO_2
    - Anaerobic – CAHs are dechlorinated
    - Mildly Reduced – Low-chlorinated CAHs (VC and DCE) can be oxidized

Enhanced Bioremediation Technologies:
Outline

I. Overview of Microbiology
II. Respiratory Processes and Metabolism
III. Biotreatment of Major Groundwater Contaminants
IV. Biodegradation/Biotransformation of Chlorinated Aliphatic Hydrocarbons (CAH)
   A. Reductive Dechlorination
   B. CAH as a Growth Substrate
   C. Aerobic Cometabolism
   D. Summary of CAH Biodegradation
V. Anaerobic/Aerobic Technologies and Applications
VI. Case Histories
VII. Tech Transfer (SOW, Cost Estimator, Design Manual, TDS)

Enhanced Bioremediation Technologies:
Biodegradation/Biotransformation of CAH

- CAH biodegradation mechanisms
  - Reductive Dechlorination
  - CAH as a growth substrate
  - Aerobic Cometabolism
  - Summary of CAH Biodegradation

Enhanced Bioremediation Technologies:
Biodegradation/Biotransformation of CAH

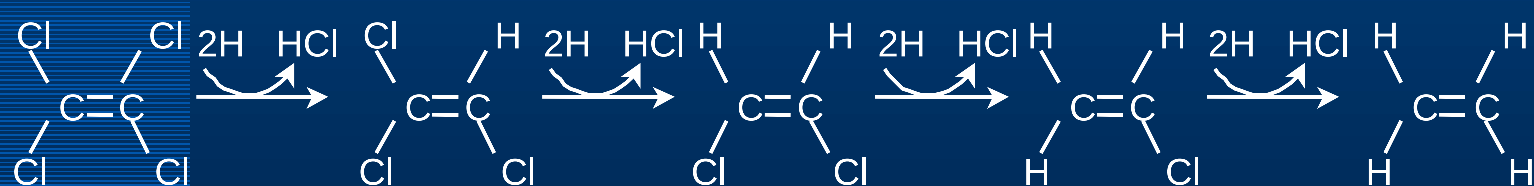
- Reductive Dechlorination
  - Halorespiration: CAH is used as an electron acceptor
  - Process requires an external electron donor
    - Lactate, propionate, butyrate
    - Glucose, sugar beet waste, molasses
    - H_2
  - CAH gains an electron and is reduced (e.g., reductive process)
  - Chlorines are removed from CAH (e.g., dechlorination)

Enhanced Bioremediation Technologies:
Biodegradation/Biotransformation of CAH

- Reductive Dechlorination (sequential process)

$2\ \text{Lactate} \rightarrow 4H_2$

$$\text{PCE} \xrightarrow{4H_2} \text{ethene} + 4H^+ + 4Cl^-$$



PCE TCE DCEs VC ETH

Enhanced Bioremediation Technologies:
Biodegradation/Biotransformation of CAH

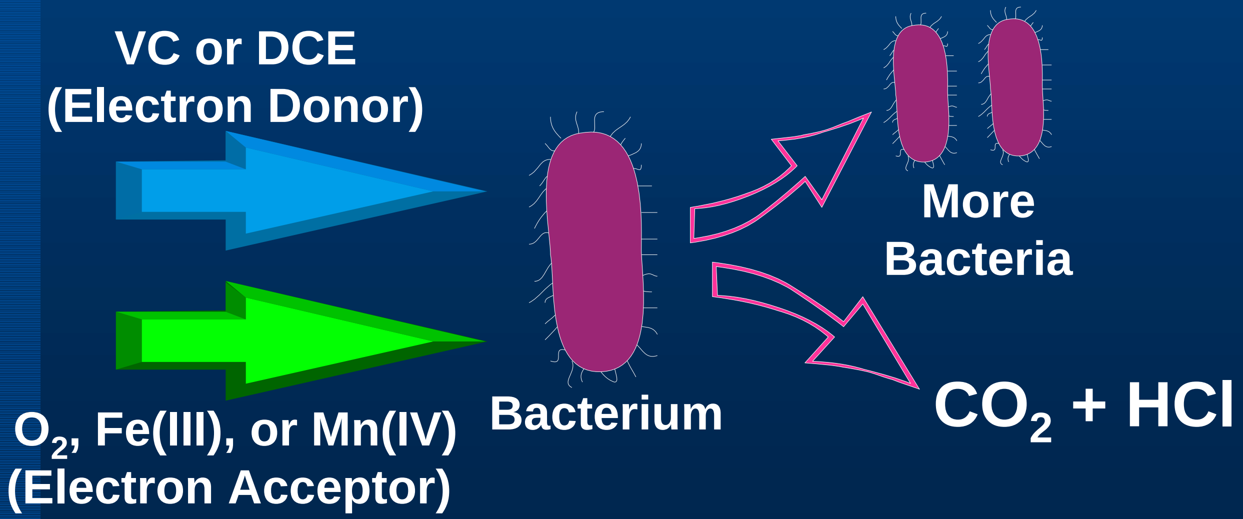
- Reductive Dechlorination
  - Requires very reduced conditions (methanogenic is ideal)
  - Kinetics (dechlorination rates)
    - Fastest for PCE dechlorination to TCE and c-DCE
    - Slowest for VC dechlorination to ethene
  - Requires an adequate supply of electron donor
  - May require extensive acclimation (months or longer)
  - Potential incomplete dechlorination end points: DCE and VC (because of different limiting factor: bacteria type)

Enhanced Bioremediation Technologies:
Biodegradation/Biotransformation of CAH

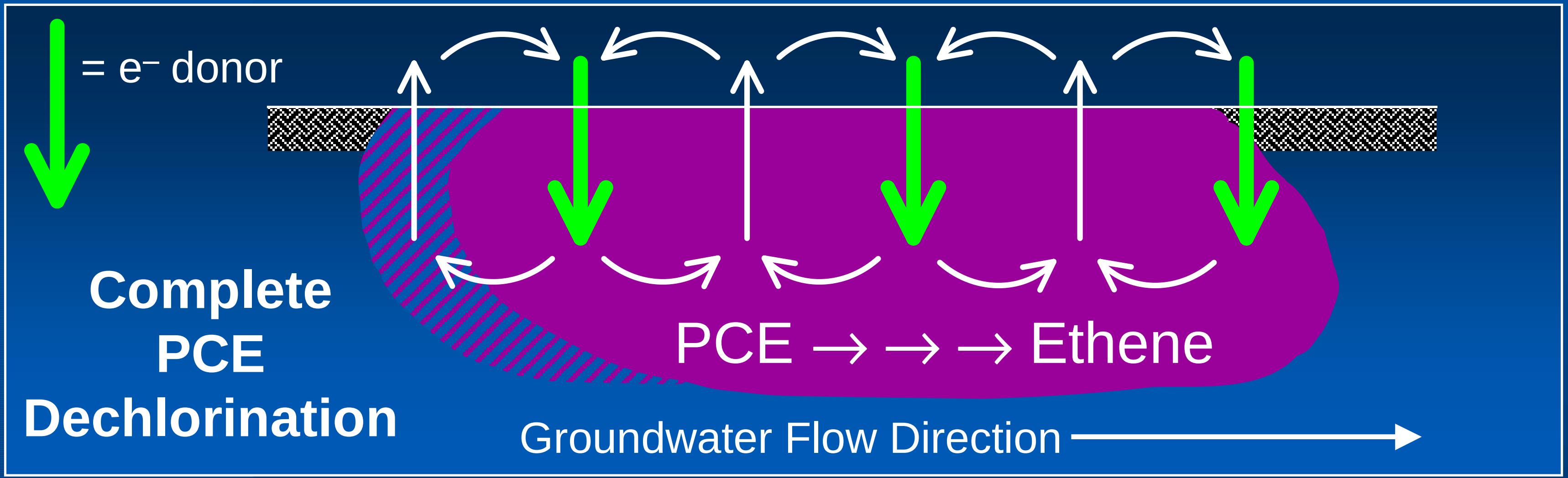
- CAH biodegradation mechanisms
  - Reductive Dechlorination
  - CAH as a growth substrate
  - Aerobic Cometabolism
  - Summary of CAH Biodegradation

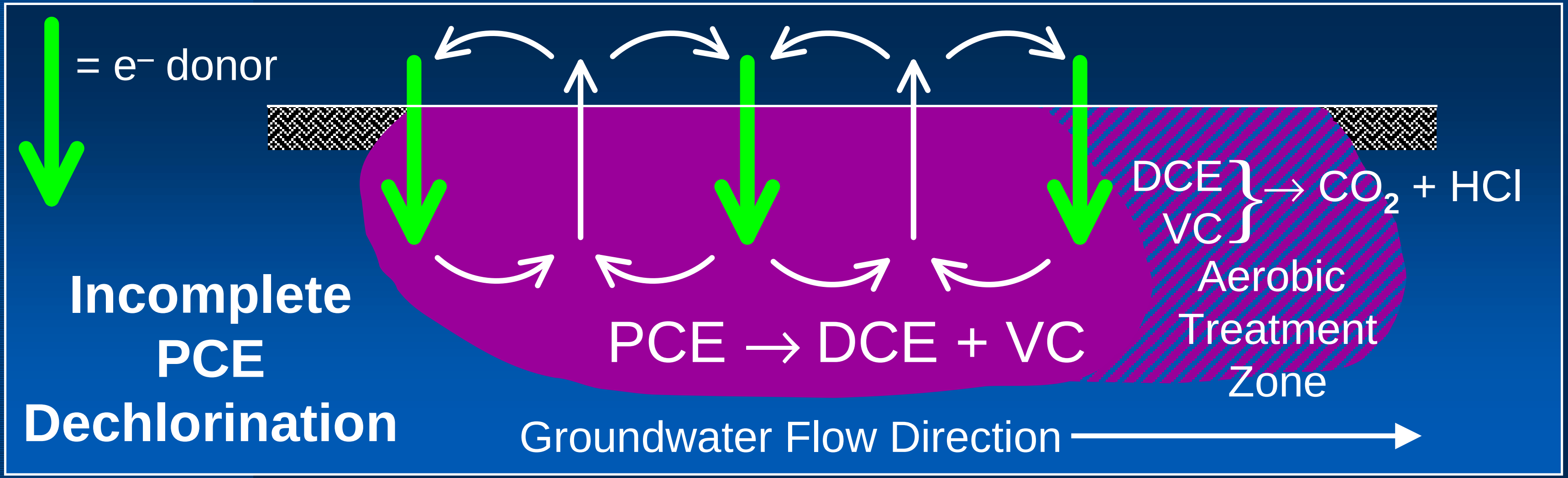
Enhanced Bioremediation Technologies:
Biodegradation/Biotransformation of CAH

- CAH as a growth substrate
  - Bacteria use CAH for Carbon and Energy
  - Limited to DCE & VC, MCA & DCAs
  - Electron Acceptors
    - Aerobic: Oxygen
    - Anaerobic: Manganese or iron-reducing conditions



Enhanced Bioremediation Technologies:
Biodegradation/Biotransformation of CAH





Enhanced Bioremediation Technologies:
Biodegradation/Biotransformation of CAH

- CAH biodegradation mechanisms
  - Reductive Dechlorination
  - CAH as a growth substrate
  - Aerobic Cometabolism
  - Summary of CAH Biodegradation

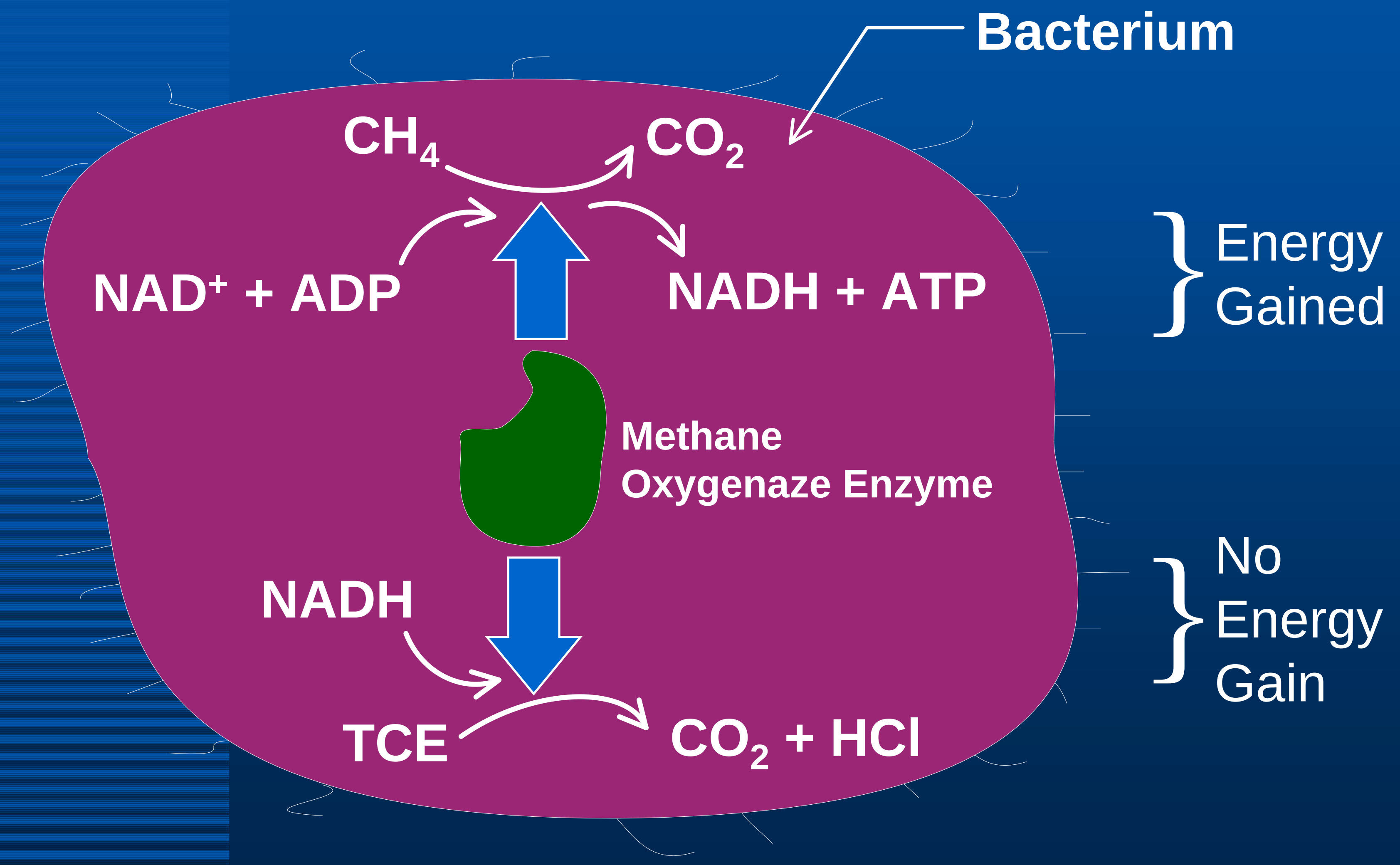
Enhanced Bioremediation Technologies:
Biodegradation/Biotransformation of CAH

- Aerobic Cometabolism
  - Bacteria use enzymes (biological catalyst) to catalyze substrate degradation
  - Non-specific enzymes
    - Cannot distinguish between a beneficial substrate and a non-beneficial substrate
    - Results in accidental (fortuitous) degradation of contaminants
  - Common contaminants amenable to cometabolism
    - TCE, DCE, VC
    - TCA, DCA
    - Chloromethanes
    - Others (e.g., MTBE)
  - PCE and Carbon Tetrachloride cannot be degraded cometabolically

Enhanced Bioremediation Technologies:
Biodegradation/Biotransformation of CAH

- Aerobic Cometabolism (example)
  - Methanotrophs
    - Enzyme: methane monooxygenase to oxidize CH_4
    - Non-specificity: Methane monooxygenase cannot distinguish between methane and TCE
    - Fortuitous degradation: Grow methanotrophs on methane and they accidentally degrade TCE
  - Redox reactions
    - Methane is the electron donor
    - Oxygen is the electron acceptor
    - TCE is a dead end for bacteria

Enhanced Bioremediation Technologies:
Biodegradation/Biotransformation of CAH



Enhanced Bioremediation Technologies:

Biodegradation/Biotransformation of CAH

- Aerobic Cometabolism (requirements)
  - Primary growth substrate (electron donor)
    - Gaseous: Propane & methane
    - Aqueous: Toluene, phenol, isopropyl benzene
  - Oxygen (Electron Acceptor)
  - Bacteria that can both degrade the cosubstrate and cometabolically degrade the contaminant

Enhanced Bioremediation Technologies:
Biodegradation/Biotransformation of CAH

- CAH biodegradation mechanisms
  - Reductive Dechlorination
  - CAH as a growth substrate
  - Aerobic Cometabolism
  - Summary of CAH Biodegradation

Enhanced Bioremediation Technologies:
Biodegradation/Biotransformation of CAH

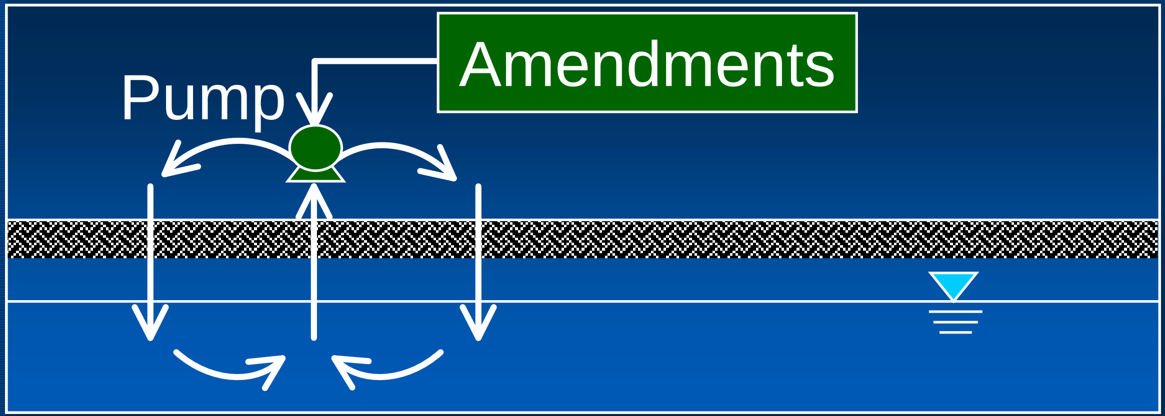
- Summary of Biodegradation Mechanisms
  - Reductive Dechlorination: CAHs can be dechlorinated under strict anaerobic conditions
  - CAH as a growth substrate: CAHs are used for carbon and energy (chloroethenes restricted to VC and DCE) under aerobic or mildly reduced conditions
  - Cometabolism: CAHs destroyed fortuitously by enzymes made to degrade a primary growth substrate

Enhanced Bioremediation Technologies:
Outline

I. Overview of Microbiology
II. Respiratory Processes and Metabolism
III. Biotreatment of Major Groundwater Contaminants
IV. Biodegradation/Biotransformation of Chlorinated Aliphatic Hydrocarbons (CAH)
V. Anaerobic/Aerobic Technologies and Applications
   A. Technology Descriptions
   B. Applicability of Aerobic Technologies
   C. Advantages and Disadvantages
VI. Case Histories
VII. Tech Transfer (SOW, Cost Estimator, Design Manual, TDS)

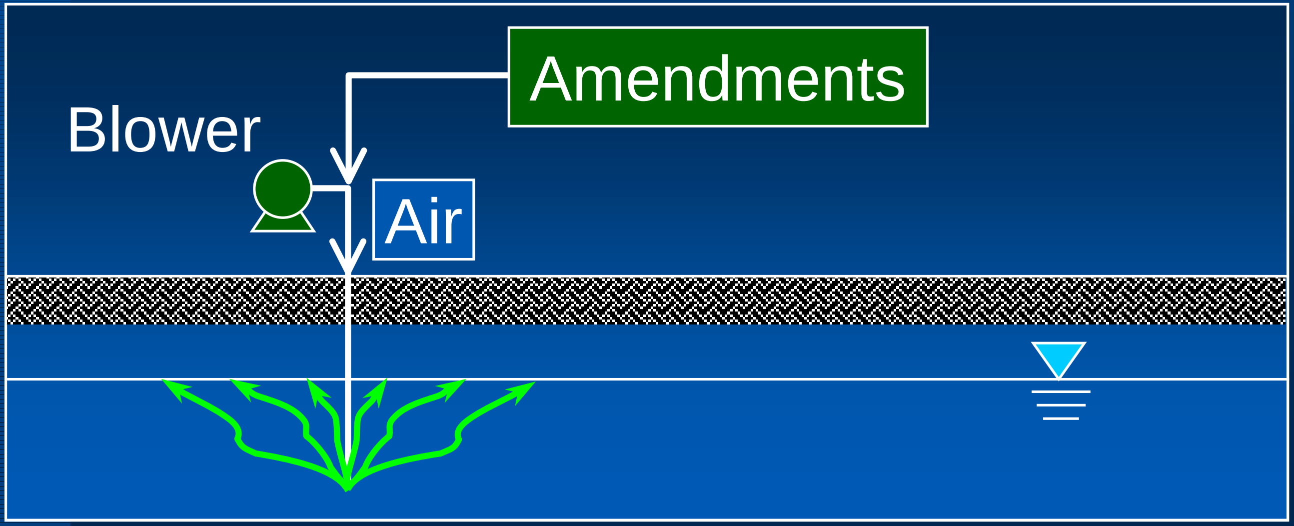
Enhanced Bioremediation Technologies:
Aerobic Technologies and Applications

- Extract-(Treat)-Reinject (ETR)
  - Pump and Treat: Aboveground treatment plus groundwater aeration
  - In Situ Cometabolism: Delivery of dissolved oxygen source and enzyme- inducing substrate (phenol, etc.) (regulations may require aboveground treatment)
  - Enhanced Anaerobic Dechlorination: Delivery of an electron donor (regulations may require aboveground treatment)



Enhanced Bioremediation Technologies:
Aerobic Technologies and Applications

- **Sparging:**
  - **Cometabolic Air Sparging:** Delivery of oxygen-containing gas with enzyme-inducing growth substrate (e.g., methane or propane)
  - **Anaerobic Sparging** (Innovative): Delivery of an inert gas (N_2 or Ar) with low (<2%) H_2 levels



Enhanced Bioremediation Technologies:
Aerobic Technologies and Applications

- Advantages of Aerobic Technologies
  - Contaminants are completely oxidized to CO_2
  - Sparging and other aerobic applications are well understood
  - O_2 is an inexpensive electron acceptor
- Disadvantages of Aerobic Technologies
  - Cannot be used for PCE or Carbon Tetrachloride
  - Limited radius of influence
    - Sparging <15 ft
    - Pump and Treat depends on the aquifer hydraulic conductivity
  - May negatively affect natural dechlorination
  - Iron precipitation may clog formation

Enhanced Bioremediation Technologies:
Anaerobic Technologies and Applications

- Advantages of Anaerobic Technologies
  - Have the potential to dechlorinate to non-toxic byproducts
  - Microbiology is well understood
  - Some compounds (PCE & CT) can only be dechlorinated
  - Some sites already are anaerobic
- Disadvantages of Anaerobic Technologies
  - Primary disadvantage: Potential incomplete dechlorination
    - Can result in VC production
  - Distribution of electron donor is a major challenge
  - Electron donor must overcome competing electron acceptors

Enhanced Bioremediation Technologies:
Steps Toward Implementation

- Establish site conditions and types of contaminants present
- Identify suitable treatment processes
- Conduct bench-scale treatability studies to validate biological process
- Perform field pilot study to validate technology and collect pertinent scale-up information
- Design full-scale system
- Gain regulatory approval
- Implement treatment process
- Conduct performance monitoring and long-term monitoring

Enhanced Bioremediation Technologies:
Major Cost Components of Each Technology

- Bench-scale studies
- Pilot-scale studies
- Design
- Reporting requirements
- Regulatory approval process
- Installation
- Substrates and nutrients
- Performance monitoring
- Long-term monitoring
- Site closure

Enhanced Bioremediation Technologies: Outline

I. Overview of Microbiology

II. Respiratory Processes and Metabolism

III. Biotreatment of Major Groundwater Contaminants

IV. Biodegradation/Biotransformation of Chlorinated Aliphatic Hydrocarbons (CAH)

V. Anaerobic/Aerobic Technologies and Applications

VI. Case Histories
   - A. Cometabolic Air Sparging at McClellan AFB
   - B. Reductive Dechlorination at Alameda Point

VII. Tech Transfer (SOW, Cost Estimator, Design Manual, TDS)

Case History: Cometabolic Air Sparging (CAS) at McClellan AFB to Remediate Chloroethene-Contaminated Aquifers

Conducted by Battelle Memorial Institute

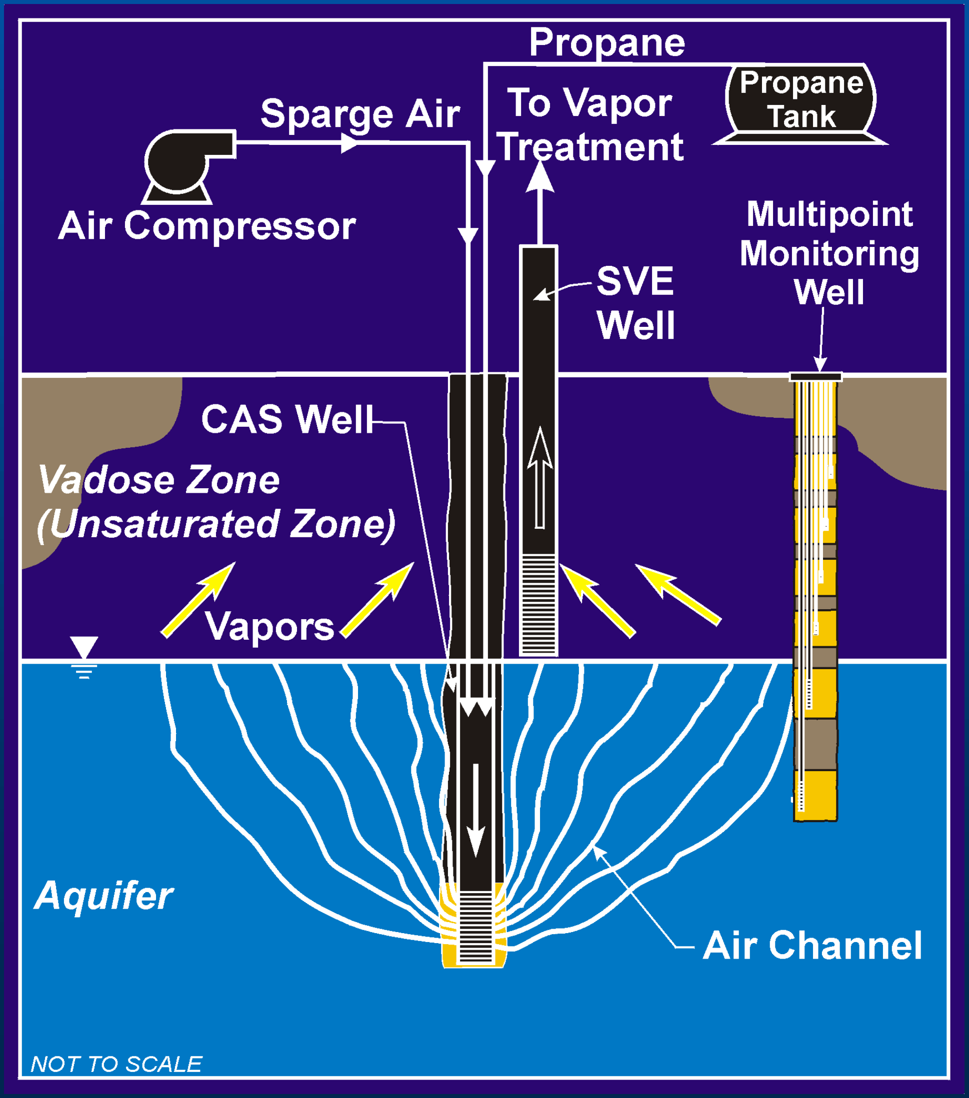
In Conjunction with:
U.S. Air Force, Environics (AFRL-MLQE)

and Oregon State University (OSU)

Funding: Environmental Security Testing and Certification Program (ESTCP)

Case History: Cometabolic Air Sparging

Conceptual Design of Cometabolic/In Situ Air Sparging



Case History: Cometabolic Air Sparging

Impacted Area and Surroundings

- COCs include solvents (TCE and DCE) in soil and groundwater
- Southeastern portion of the base (555 acres)
- Engine repair shops, plating shops, washracks, industrial waste line, above- and belowground storage tanks, runway access, disposal pits
- Two major groundwater and five soil-gas plumes identified
- Groundwater plumes extend approximately 1,750 feet off base to the east (Controlled by P&T system)
- Groundwater table is 110 ft bgs

Case History: Cometabolic Air Sparging

Site Histories

Contaminant Concentrations

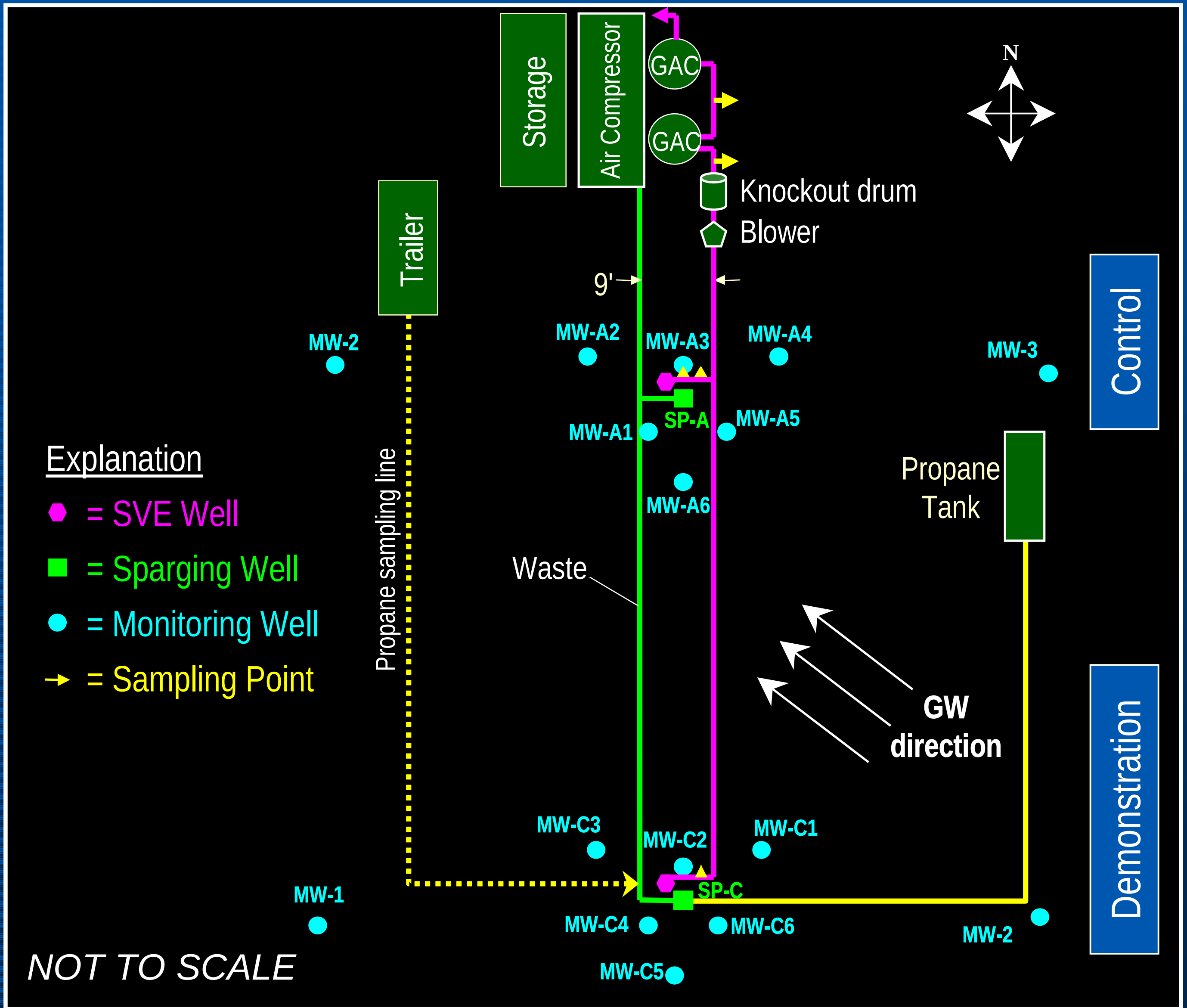
- Major Groundwater Contaminants
  - TCE <1,000 µg/L; *c*-DCE <600 µg/L
- Minor Groundwater Contaminants
  - PCE <2.5 µg/L
  - 1,1- and *t*-DCE <10 µg/L
  - 1,1-DCA <10 µg/L
- Soil Gas Contaminants
  - TCE <800 µg/L
  - *c*-DCE <400 µg/L

Unique or Confounding Site Characteristics

- Tight soil matrix
  - Heterogeneities lead to uneven distribution of air
- Nutrient limitations
  - Low nitrate (≈ 5 mg/L)
- Propane-degrading bacteria
  - Low number of bacteria, require acclimation for growth

Case History: Cometabolic Air Sparging

Demonstration Layout



Case History: Cometabolic Air Sparging
Sparge and SVE Well Details

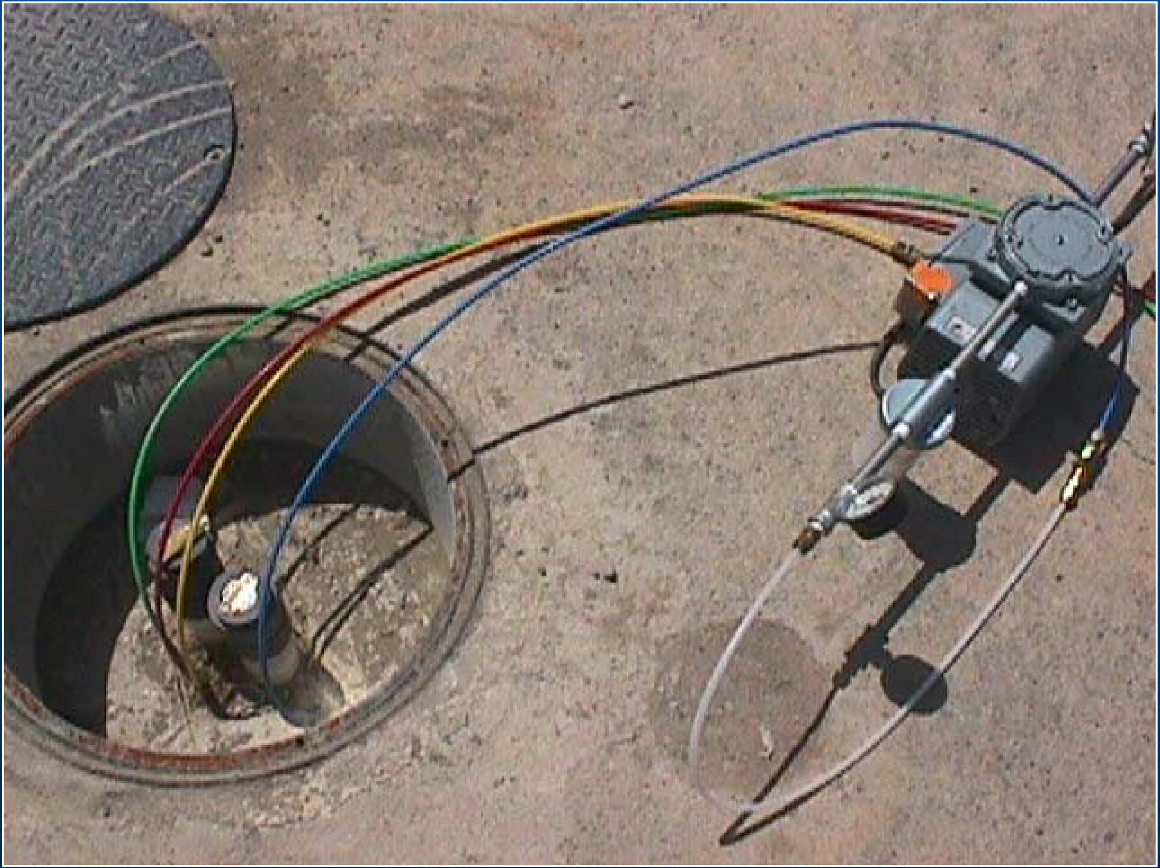
Case History: Cometabolic Air Sparging

Propane-Fed Zone, Looking North

Case History: Cometabolic Air Sparging

Multilevel Monitoring Well

- 2 groundwater monitoring points (113 & 117 ft bgs)
- 4 soil gas points (30, 65, 85, 95 ft bgs)

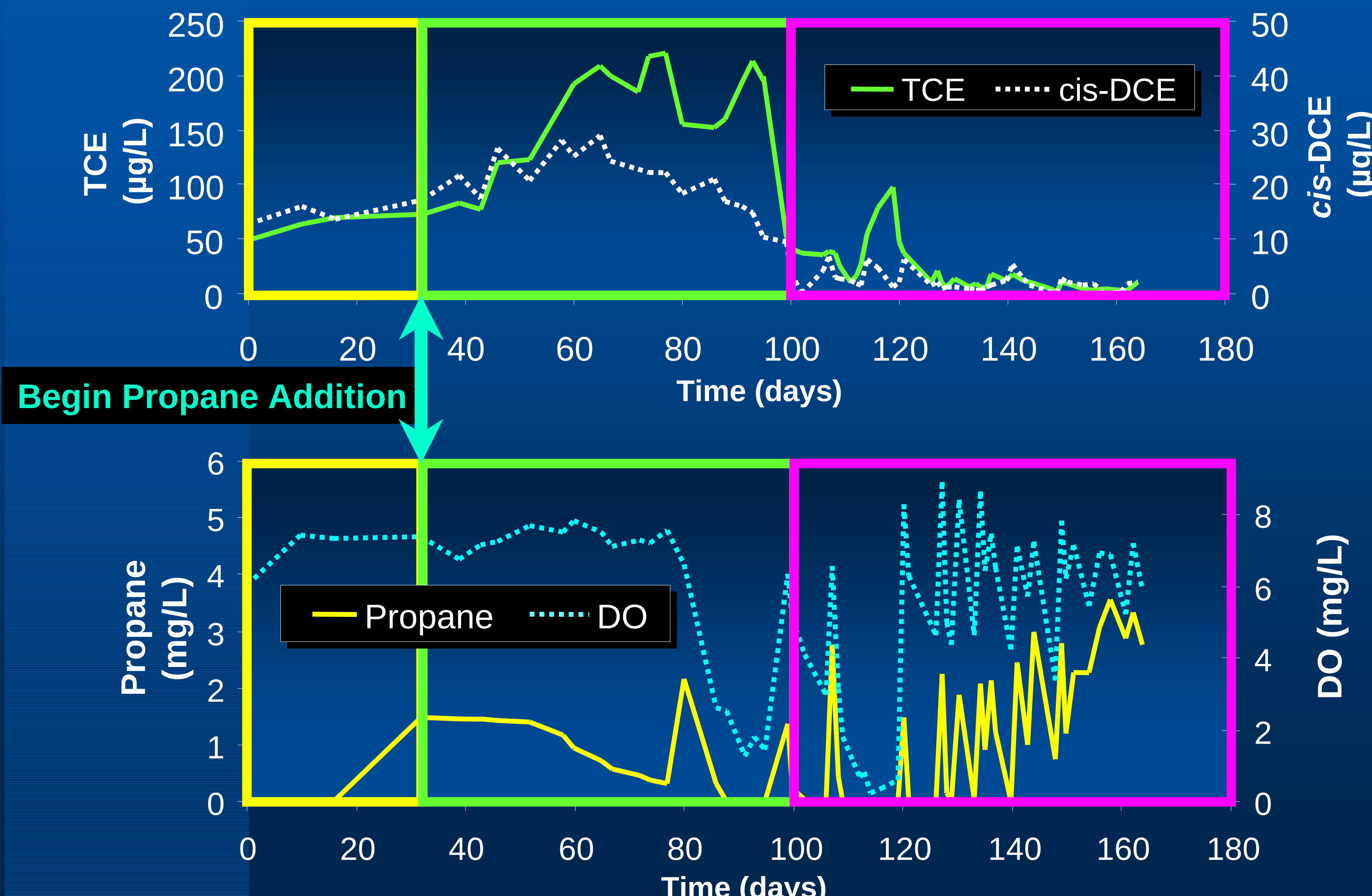


Case History: Cometabolic Air Sparging

Propane Addition to Groundwater

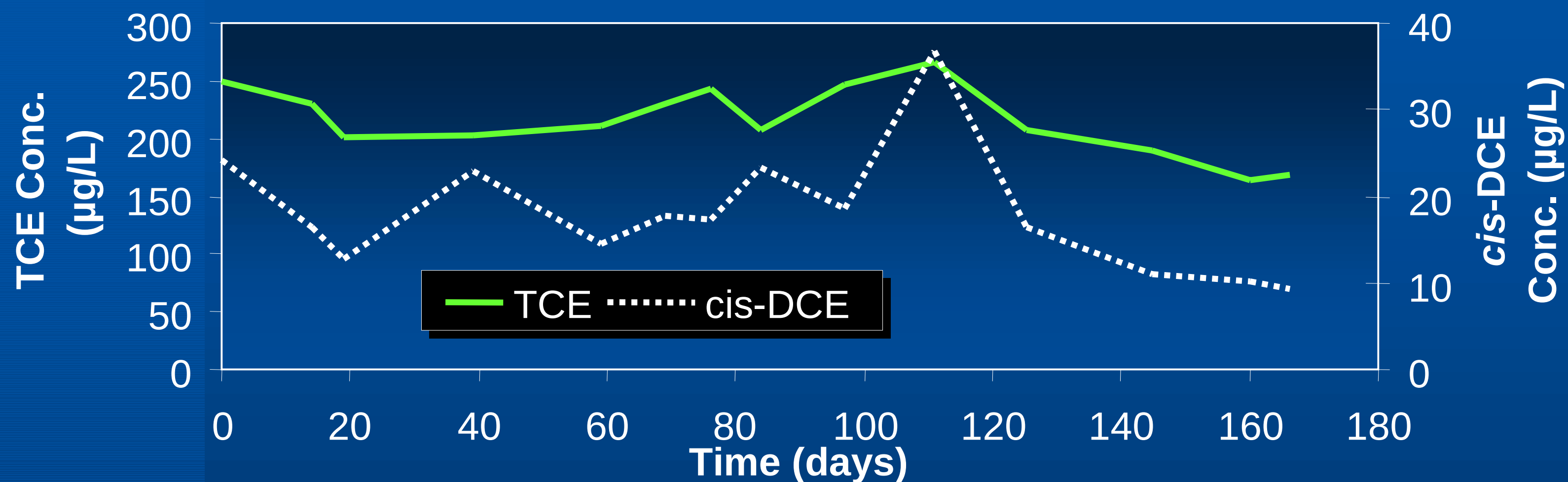
- Sparge rate = 10 scfm/well
- 2% propane added intermittently to the Demonstration Zone
- Groundwater monitored for
  - Propane, DO, TCE, *c*-DCE
- Soil gas monitored for
  - Propane, TCE, and *c*-DCE, O_2
- 1-month instrument calibration and testing required
- Propane addition began on day 36

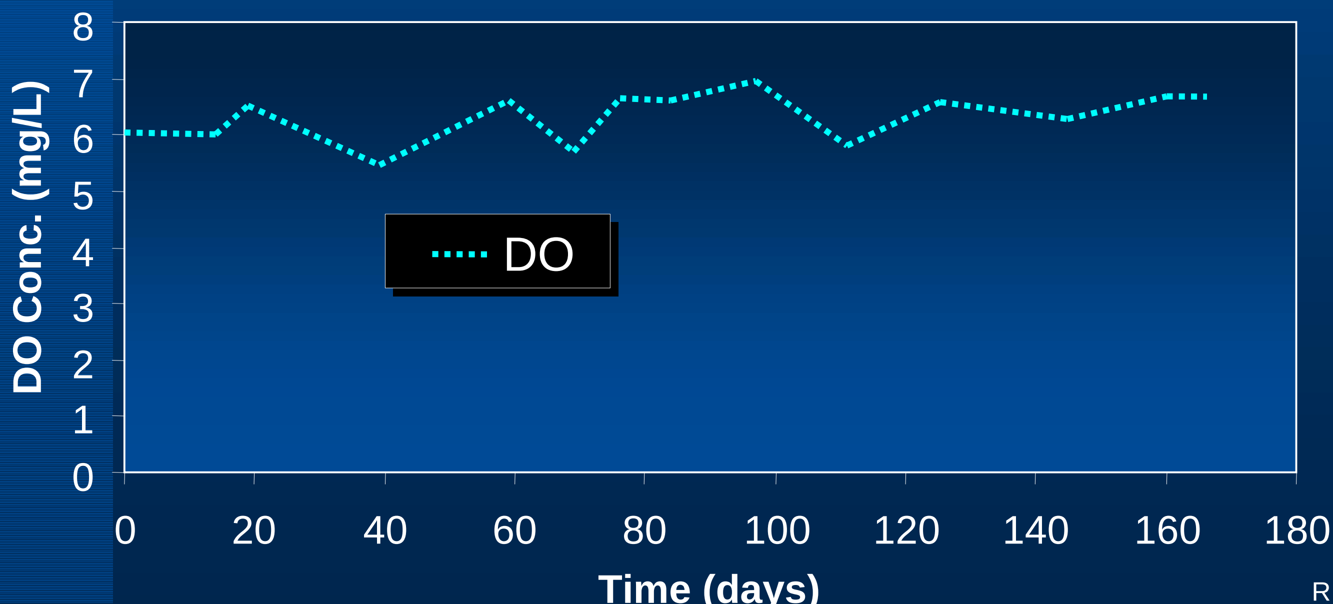
Case History: Cometabolic Air Sparging
Active Zone at C2-117 ft (MW-C2-GW2)



Case History: Cometabolic Air Sparging

Control Zone at A3-117 ft (MW-A3-GW2)





Case History: Cometabolic Air Sparging

Stimulation of Propane-Degrading Bacteria

- Acclimation of propane-degrading bacteria
  - Required about 40 to 50 days
  - Similar to laboratory microcosm studies
  - Stimulation occurred without NO_3^- addition
- Pulsed additions of air and propane for over 100 days led to effective TCE and *c*-DCE removal in the saturated zone where effective propane delivery and uptake occurred
- No TCE or *c*-DCE degradation in wells not fed propane
- No TCE or *c*-DCE degradation in the control site

Case History: Cometabolic Air Sparging

Lessons Learned

- Demonstrated the use of propane to promote the cometabolic degradation of TCE and *c*-DCE
- Air Sparging without propane did not effectively remove TCE and *c*-DCE
- Background nitrate concentrations insufficient to maintain propane and TCE degradation

Case History: Cometabolic Air Sparging

Lessons Learned

- Addition of ammonia to sparge gas ongoing
- Process optimization will be explored in Spring 2000
- Investigate vadose zone activity
- Add nitrogen (NH_4^+) to the vadose zone
- Simplify pilot testing approach
  - Fewer monitoring wells
  - Reconsider need for a control site

Case History: Cometabolic Air Sparging

Points of Contact

- Cathy Vogel (ESTCP)
  - (703) 696-2118
  - vogelc@acq.osd.mil
- Alison Lightner (AFRL-MLQE, Tyndall AFB)
  - (850) 283-6303
  - Alison.lightner@mlq.afrl.af.mil
- www.estcp.org\projects\cleanup\index.htm
- Victor Magar (Battelle Principal Investigator)
  - (614) 424-4604
  - magarv@battelle.org

Case History: Treatability Test for In Situ Anaerobic Dechlorination at Alameda Point (formerly Alameda Naval Air Station)

Conducted by Battelle Memorial Institute

In Conjunction with: U.S. Air Force, Environics (AFRL-MLQE),

Naval Facilities Engineering Service Center (NFESC),

Cornell University,

and U.S. Environmental Protection Agency (USEPA)

Funding: Environmental Security Testing and Certification Program (ESTCP)

Case History: In Situ Anaerobic Dechlorination

Technology Application

- Site was selected as one of 5 sites for validation of enhanced anaerobic dechlorination:
  - Reductive Anaerobic Biological In Situ Treatment Technology (RABITT)
  - Navy support, Regulatory approval, suitable site logistics

Case History: In Situ Anaerobic Dechlorination

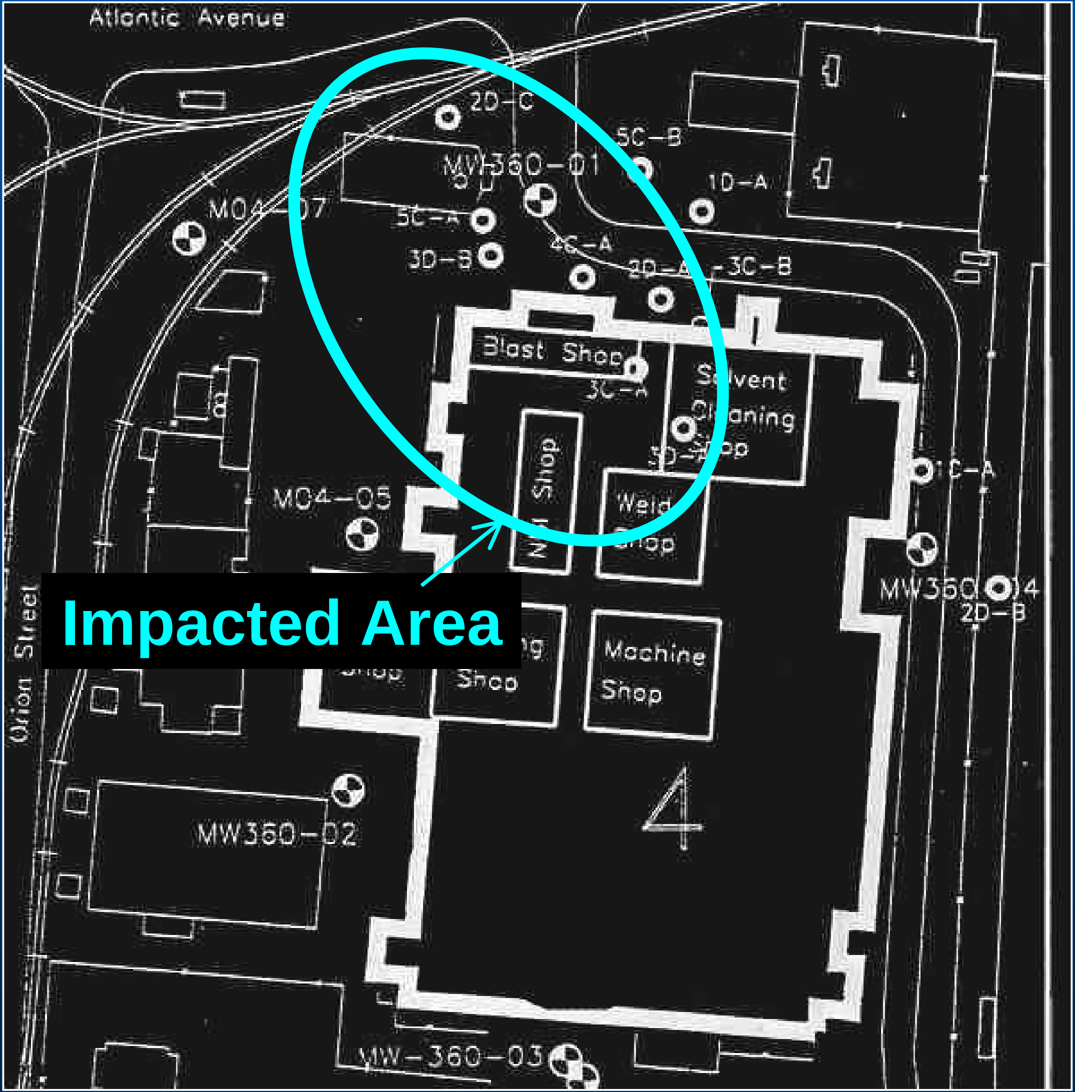
Background – Site History

- DNAPLs found in groundwater under repair shop

Contaminant	Maximum Concentration (µg/L)
TCE	24,000
DCE	8,600
VC	2,200
Ethene	Not reported

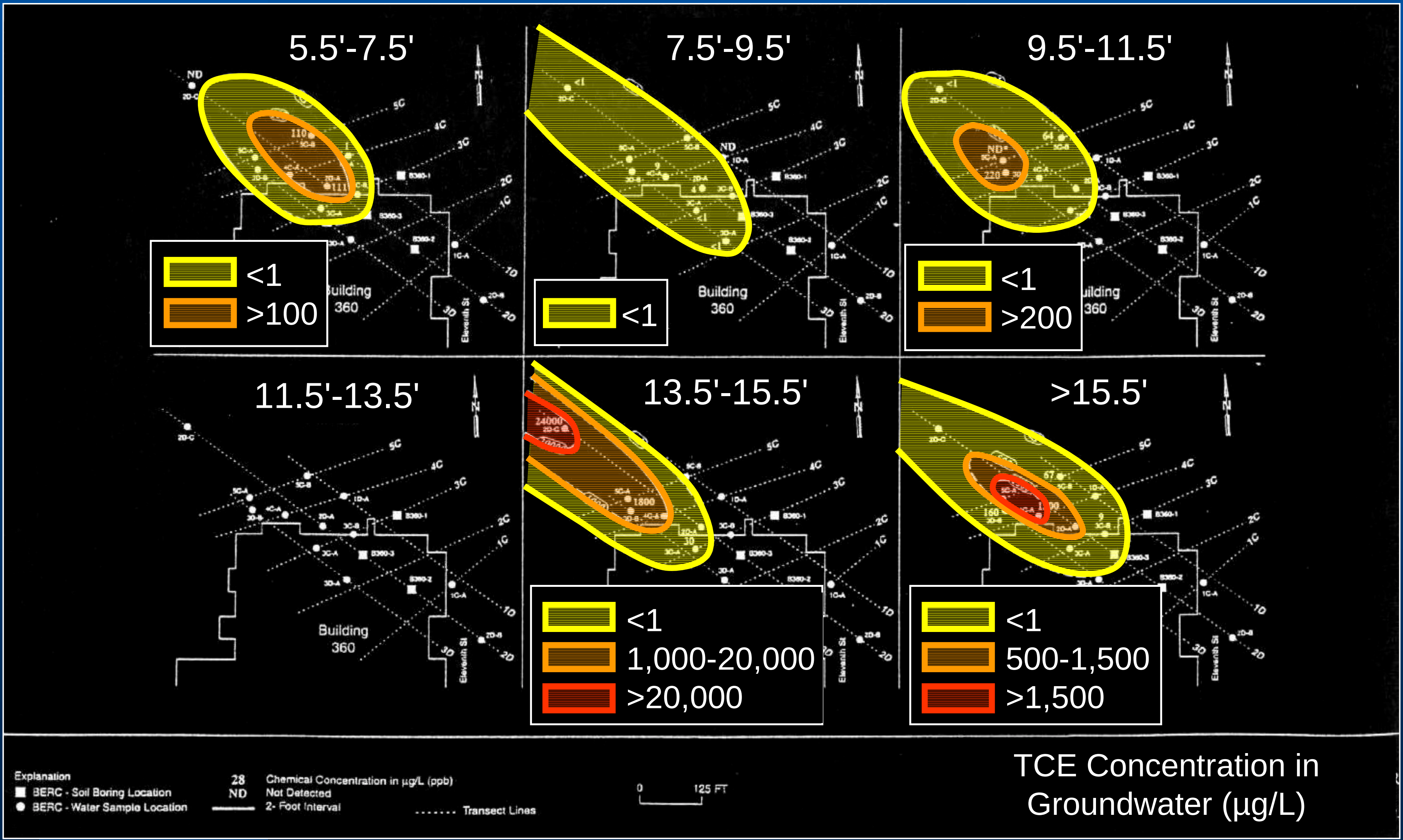
Case History: In Situ Anaerobic Dechlorination

Site Map



Case History: In Situ Anaerobic Dechlorination

Site Map (Impacted Area)



Case History: In Situ Anaerobic Dechlorination

Site 4: Characterization Data

- Hydrogeology
  - 0 to 7 ft bgs: Sand and gravel fill
  - 7 to 28 ft bgs: Fine to medium sands with varying amounts of clay and silt
  - Depth to groundwater: 4 to 6 ft bgs
  - hydraulic conductivity ≈ 10^{-3} cm/sec
- Geochemistry
  - Dissolved oxygen < 1.0 mg/L
  - Sulfate: ~300 mg/L
  - Dissolved methane < 0.1 mg/L
  - DOC: ~120 mg/L
  - pH between 7.0 and 7.8
  - Total alkalinity 0.013 eq/L
- Contaminant Profile
  - Daughter products present indicating reductive dechlorination occurring naturally, but slowly

Case History: In Situ Anaerobic Dechlorination
Microcosm Study

- Electron Donors:
  - Yeast Extract (200 mg/L)
  - Propionate (1.5 mM)
  - Lactate (3 mM)
  - Butyrate (3 mM)
  - Lactate/Benzoate (1.5 mM each)
- All donors show conversion of TCE to ethene after 162 days of incubation
- Butyrate shows the most consistent and rapid conversion of TCE to ethene

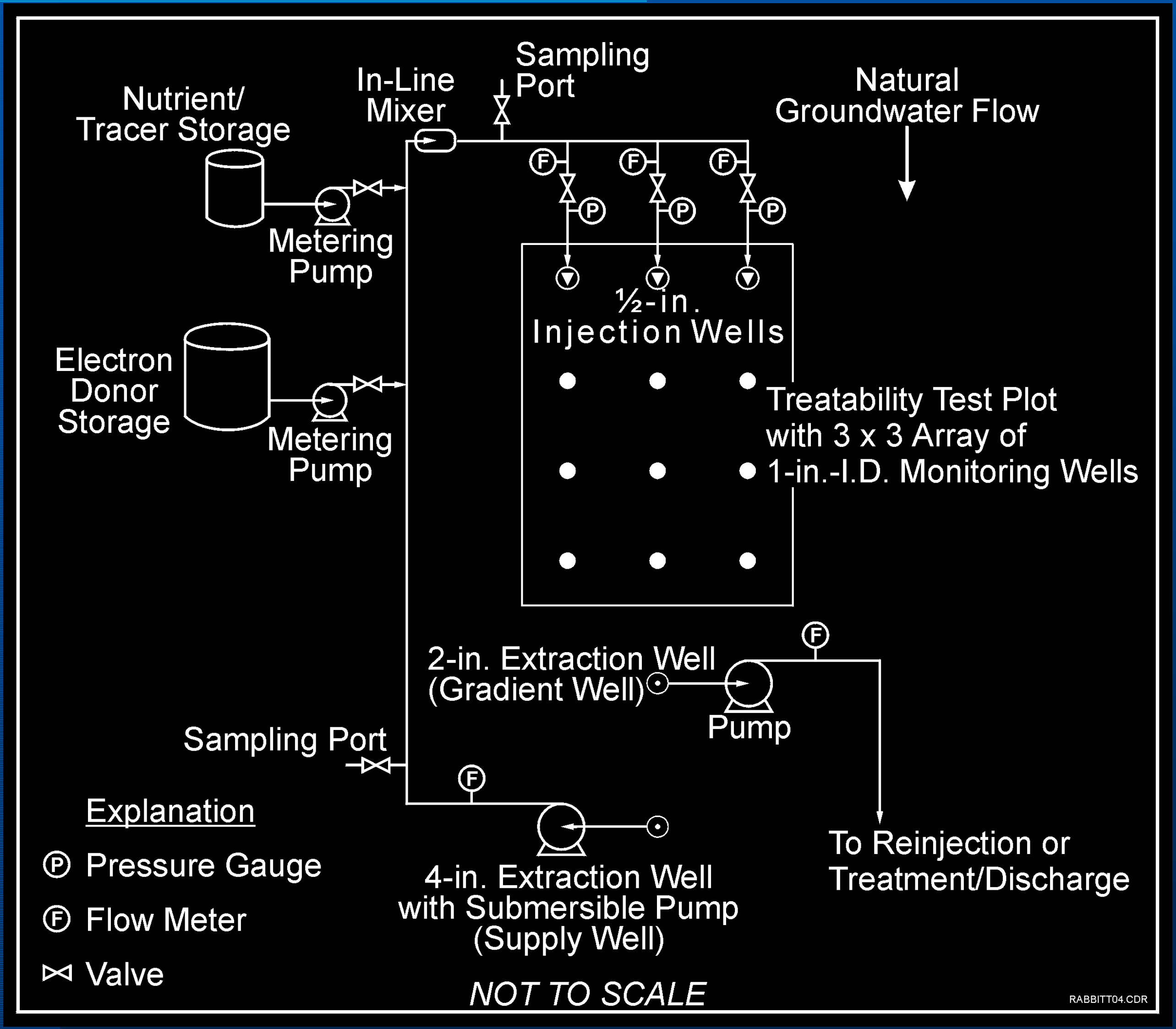
Case History: In Situ Anaerobic Dechlorination

System Design

- Three ½-in. injection wells screened from 24 to 27 ft
- Nine 1-in. monitoring wells screened from 25 to 26.5 ft
- One 4-in. extraction (supply) well screened from 13 to 16 ft
- One 2-in. hydraulic gradient control well screened from 24 to 27 ft
- One 2-in. background well screened from 24 to 27 ft
- Plot dimensions: 3 x 20 ft
- Associated aboveground components

Case History: In Situ Anaerobic Dechlorination

System Design (plan view)



Case History: In Situ Anaerobic Dechlorination

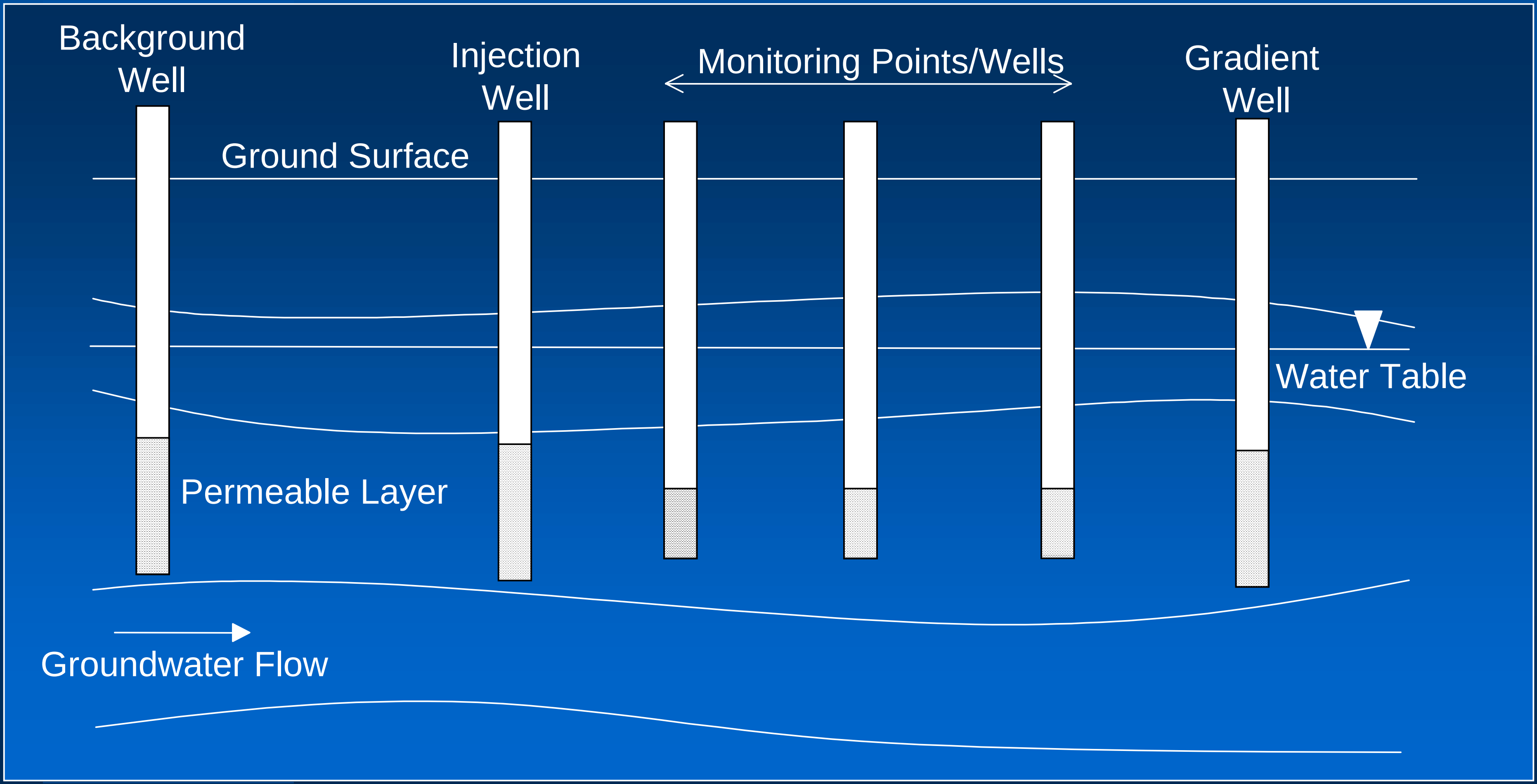
Site Layout: Injection Wells

Case History: In Situ Anaerobic Dechlorination

Site Layout: Monitoring Wells

Case History: In Situ Anaerobic Dechlorination

System Design (Profile View)



Case History: In Situ Anaerobic Dechlorination
Design Criteria

Total System Pumping Rate: 0.62 L/min (236 gal/day)

- Stock Solution 1: Tracer and pH buffer
  - Stock Concentrations:
    - [NaBr] = 5.8 g/L
    - [$NaHCO_3$] = 85 g/L
  - Target In Situ Concentration
    - [NaBr] = 100 mg/L
    - [$NaHCO_3$] = 1.6 g/L
  - Feed Rate: 12 mL/min
- Stock Solution 2: Electron donor and nutrients
  - Stock Concentrations:
    - [Butyric Acid] = 1.25 M
    - [Yeast Extract] = 8.3 g/L
  - Target In Situ Concentrations:
    - [Butyric Acid] = 3 mM
    - [Yeast Extract] = 20 mg/L
  - Feed Rate: 1.5 mL/min

Case History: In Situ Anaerobic Dechlorination
Monitoring Parameters

- Geochemical Parameters
  - DO
  - nitrate
  - Fe(II)
  - sulfate
  - methane
  - VFAs
  - pH
  - temperature

- Contaminants & Daughter Products
  - PCE
  - TCE
  - DCEs
  - vinyl chloride
  - ethene
  - ethane

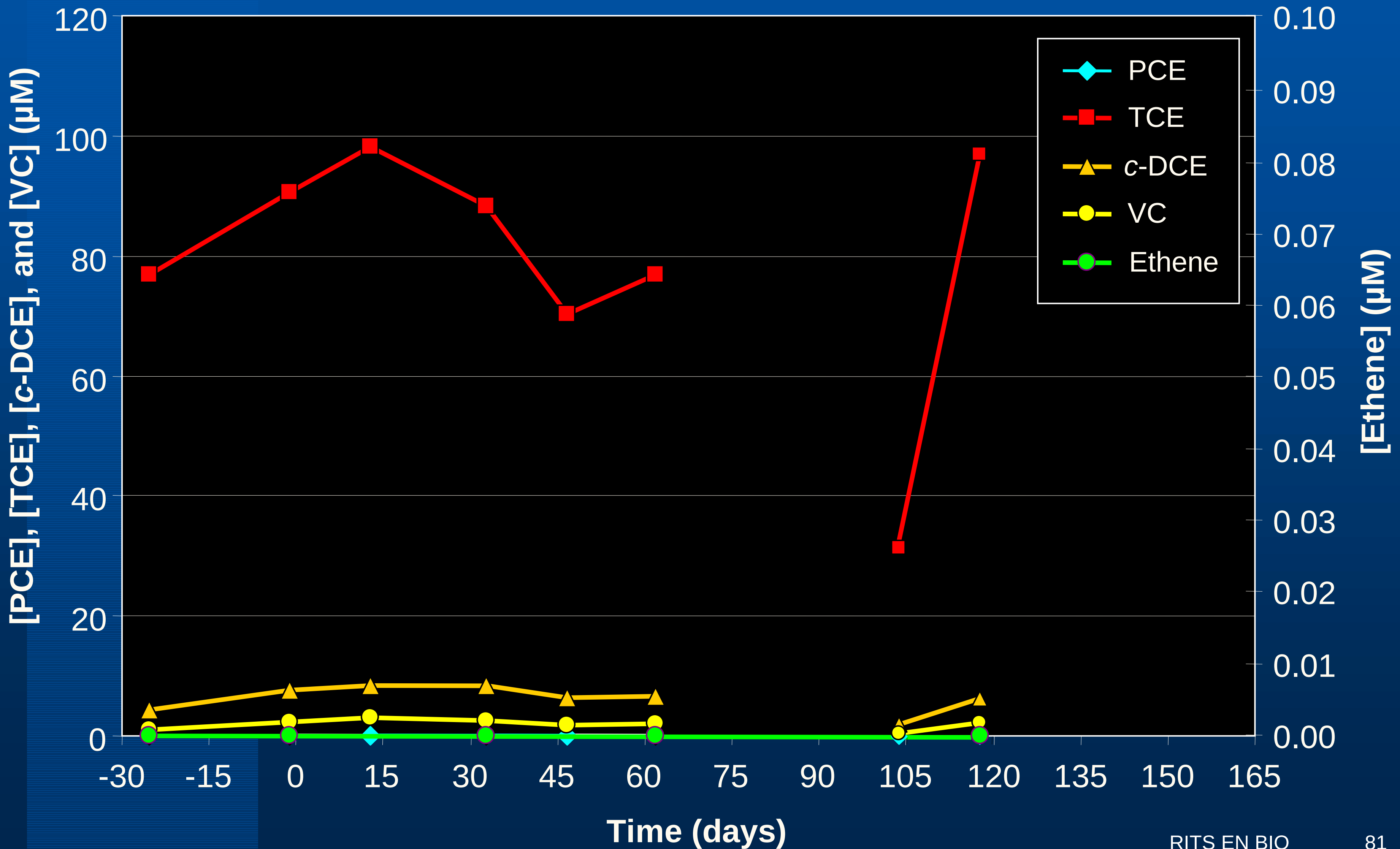
- Process Measurements
  - bromide
  - flow rates
  - injection pressures

Case History: In Situ Anaerobic Dechlorination
Observations

- TCE transformed to *cis*-DCE, VC, and ethene
- Bromide tracer distributed throughout testing zone
- Redox potential depressed (~ –200 mV)
- Biological indicators
  - Electron Acceptors
    - Decreases in oxygen and nitrate
    - Increases in Fe(II) observed
    - Sulfate fluctuating
  - Methane production observed

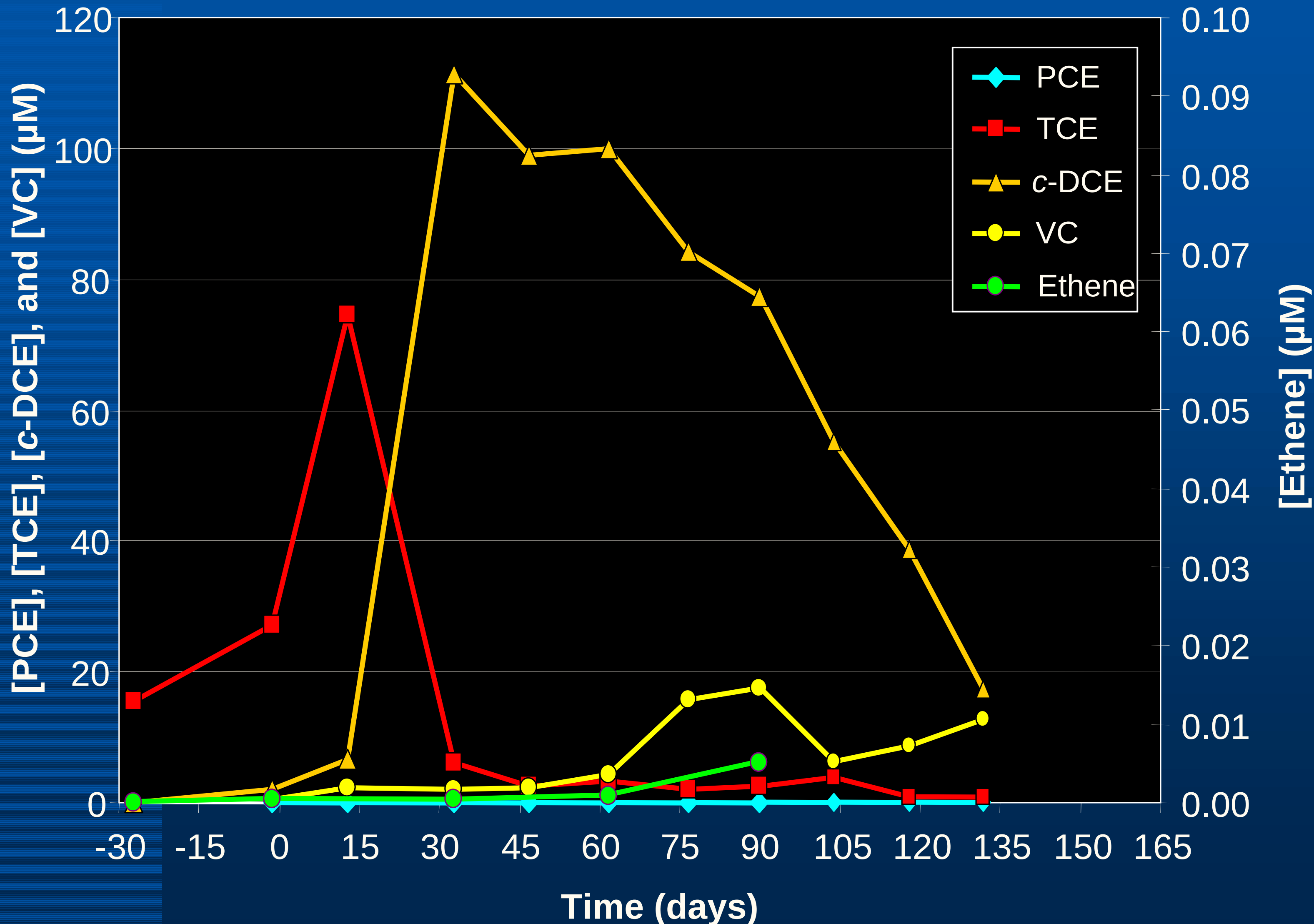
Case History: In Situ Anaerobic Dechlorination

Chloroethene Profile: Injected Water



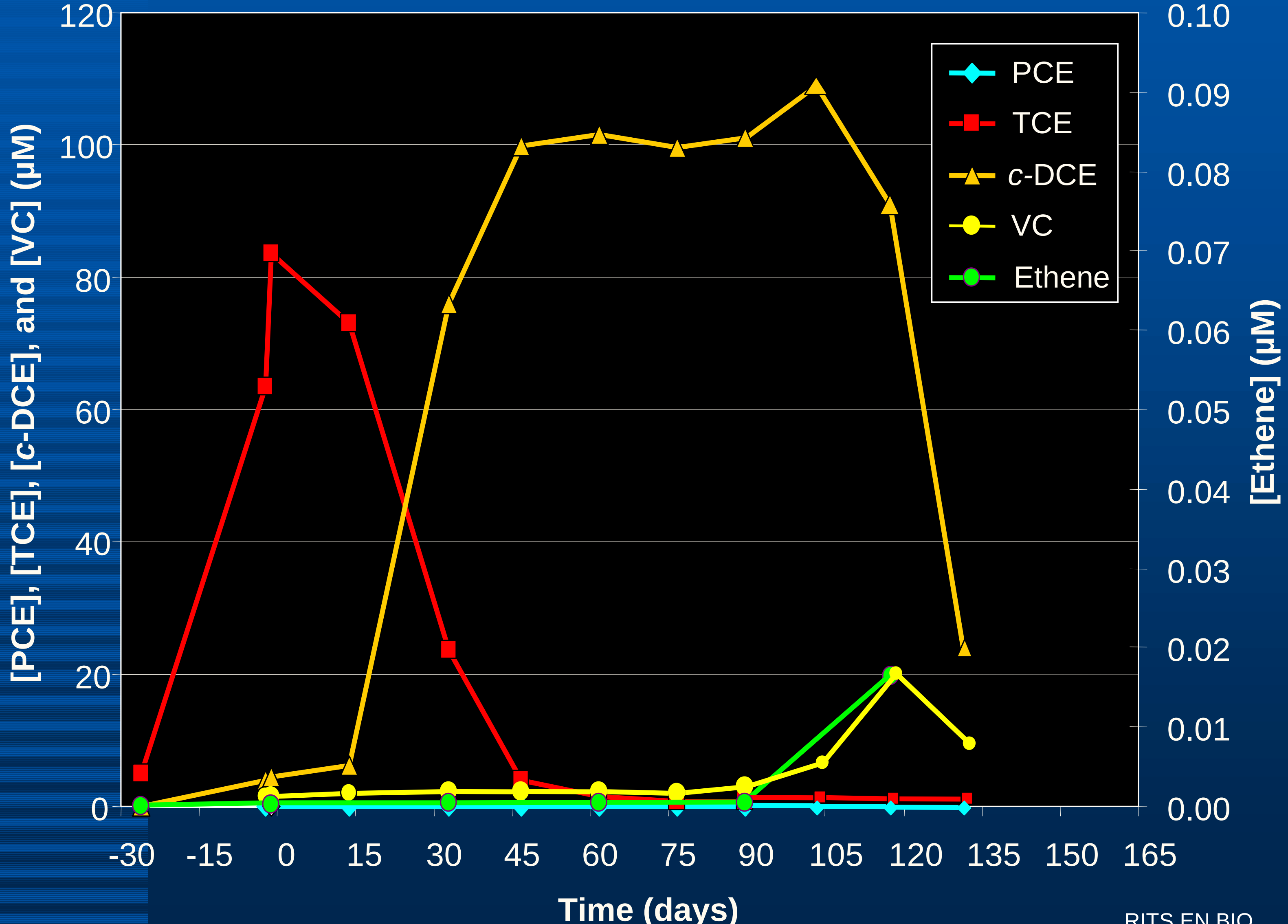
Case History: In Situ Anaerobic Dechlorination

Chloroethene Profile: 5 Feet from Injection



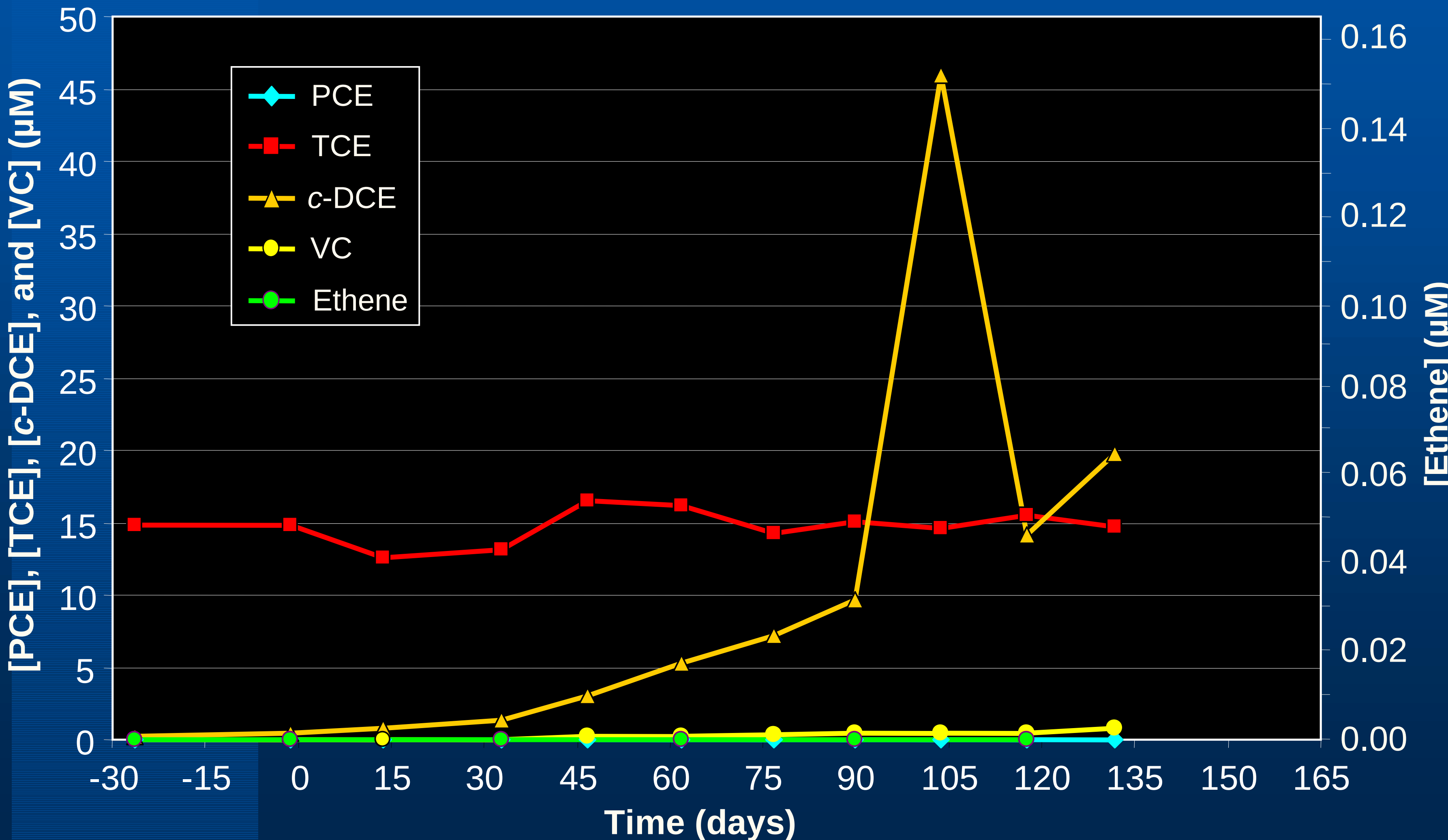
Case History: In Situ Anaerobic Dechlorination

Chloroethene Profile: 10 Feet from Injection



Case History: In Situ Anaerobic Dechlorination

Chloroethene Profile: 15 Feet from Injection



Case History: In Situ Anaerobic Dechlorination
Lessons Learned

- Biologically catalyzed reductive dechlorination can be stimulated at Alameda Point, Site 4
- Reduction of TCE proceeds to ethene
- Delivery of substrate at a large scale may run into challenges due to a less hydraulically conductive layer present at approximately 15 ft bgs

Case History: In Situ Anaerobic Dechlorination

Points of Contact (EFA or EFD)

- Ron Hoeppel (NFESC)
  - Phone: (805) 982-1655
  - e-mail: hoeppelre@nfesc.navy.mil
- Patricia McFadden (EFA West)
  - Phone: (650) 244-2520
  - e-mail: pamcfadden@efawest.navfac.navy.mil
- Bruce Alleman (Battelle Principal Investigator)
  - Phone: (614) 424-5715
  - e-mail: allemanb@battelle.org